

## **EXECUTIVE SUMMARY**

**Effects of Temperature, Humidity, Nitrogen Dioxide and Nitric Acid Gases  
on Carbon-Steel, Galvanized, and Painted Steel**

**Final Report**

**Prepared for the California Air Resources Board**

**Agreement A4-109-32**

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August 1987

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## I. Introduction.

The deterioration of both natural and man-made materials exposed to the environment is inevitable. Property damage in the United States due to corrosion alone may exceed \$70 billion/year.

In part this damage may be attributable to naturally occurring conditions and the nature of the exposed materials. However, since the industrial revolution, the increased combustion of fossil fuels has added a burden of acid gases to the atmosphere. These gases, chiefly nitrogenous and sulfurous compounds, may significantly contribute to property damage.

Property damage attributable to pollutant gases constitutes part of the real cost of pollution and is important in determining the cost-to-benefit ratio of pollution control equipment.

The study of atmospheric corrosion of steel by pollutant gases is a relatively new area of study. Traditional methods for investigating atmospheric corrosion involve exposure of material to the ambient atmosphere or to a surrogate salt spray; generally changes in weight (gain or loss) is measured. The purpose of such tests is to estimate the expected life of exposed material rather than to relate cause and effect.

Modern trends in material science are directed towards direct measurements and detailing the processes involved at the molecular level under well characterized and controlled conditions. This is particularly important for atmospheric corrosion where it is necessary to relate cause and effect for economic modeling and given the complexity of the urban atmosphere.

Over 1600 trace gases have been identified in urban air with more than a dozen of these implicated in corrosion processes. Unfortunately, few studies have directly addressed the corrosion of steel by specific pollutant gases such as nitrogen dioxide ( $\text{NO}_2$ ) and nitric acid ( $\text{HNO}_3$ ).

Nitrogen dioxide is not expected to be a major corrosive agent in the atmosphere. In a laboratory study, no damage to carbon-steel was observed below 0.5 ppm  $\text{NO}_2$ . However, a strong synergistic effect was observed with sulfur dioxide present and at 50% relative humidity (RH). The synergism was not observed at 90% RH.

The objective of this study is to investigate the potential effect of  $\text{NO}_2$  and  $\text{HNO}_3$  on carbon-steel, galvanized and painted steel. This study attempts to measure initial rates of corrosion at realistically short times using techniques less ambiguous than weight loss/gain methods employed with longer exposure times.

## II. Methodology.

Surface electrode microcells were developed to directly show the effects of humidity and pollutant nitrogen dioxide and nitric acid gases on metals without requiring wetted surfaces. Corrosion is an electrochemical phenomenon and these miniature electrochemical cells measure corrosion rate more directly and more sensitively than can be done with bulk weight change. The technique used in this study is called the galvanostatic polarization method and has been used to study the corrosion of wetted metal surfaces but this is the first application to metal corrosion by gases.

Fourier transform infrared spectroscopy was used to identify surface corrosion products.

Coated galvanized steel sheet was selected for study because it is commonly used for exterior siding in residential and commercial buildings throughout the United States.

Samples were obtained through the courtesy of Marwais Steel Company, Richmond, California. Marwais receives galvanized steel sheet in coil form and applies a paint coating typical for siding applications.

### III. Results.

The effects of temperature were investigated from 10°C to 40°C with nitrogen dioxide held constant at 2.5ppm and the absolute humidity held at 0.0063 grams of water vapor per liter of air. This corresponds to approximately 71% relative humidity (at 10°C) to 12% relative humidity (at 40°C).

Within the accuracy of the data there was no observed effect of temperature in this range indicating a low energy of activation for the corrosion process.

Iron shows a reasonably strong dependence of corrosion on humidity. The polarization resistance decreases (corrosion rate increases) as humidity increases to about 60%, above which the values level off, presumably because of surface full saturation or coverage by the surface moisture film.

The polarization resistance values, from electrochemical measurements on painted and galvanized steel specimens showed only a weak dependence on humidity up to about 75%, above which the corrosion rate increased rapidly. However, the corrosion rates for the galvanized specimens are several orders of magnitude higher than for the uncoated iron specimens. For the galvanized specimens, a galvanic couple exists between the zinc coating and the adjoining steel substrate. The galvanic current is rather high and concentrated at the small surface area of zinc at the exposed edge of the coated specimen. Polarization resistance in this case measures the galvanic current passing between the two metals and is consequently low compared to the values for iron.

There was no evidence of degradation of the paint coating or undercutting of the coating in these short tests.

Nitrogen dioxide is only a mild corrodant of steel and zinc under the conditions studied. The initial rate of surface degradation is linear in nitrogen dioxide concentration. At the earliest exposure times nitrogen dioxide may weakly passivate (inhibit) corrosion by water vapor. The corrosion products included the metal oxides, nitrate ion, and for the zinc surface ammonium ion was formed as well; consistent with the strong reducing power of zinc.

Nitrogen dioxide caused no perceptable damage to the polyester/epoxy painted surfaces under the initial exposure conditions of this study.

Nitric acid gas rapidly attacked both steel and zinc surfaces producing nitrate ions, nitrite ions, and for the zinc surface ammonium ions were also formed.

There was slight degradation of the polyester/epoxy paint surface by nitric acid producing nitrate ester.

### IV. Conclusions.

An effective surface microcell has been developed to determine the effects of humidity, nitrogen dioxide, and nitric acid gases on iron and zinc surfaces. These microcells may be adaptable to field studies of corrosion if studies are conducted to determine a suitable preconditioning of the cell surface or the long term behavior of the cell without conditioning. Such devices provide the inherent advantage of measuring corrosion rate in real-time permitting a meaningful correlation between material damage and the fluctuating pollutant gas concentrations.

Infrared analysis of the surface corrosion products illustrates the nature of the surface alterations. For the pollutants used in this study ammonium salts were formed which exhibit hygroscopic properties. Hygroscopic salts, which take up water vapor from air, increase the time of wetness of exposed metal surfaces.

The mild damage to the polyester paint by nitric acid may soften the coating lowering its scratch resistance. This, in turn, would promote undercutting by corrosion.

It is important to note that this study was of initial corrosion rates which complement long term corrosion studies, and which are recommended for future studies. This data is of use in addressing the important early stages of corrosion. However, as surface coatings weather they develop protective coatings that slow the rate of attack.

The electrochemical and surface spectroscopic methods used in this study have been shown to offer distinct advantages in the study of atmospheric corrosion.

## V. Recommendations.

Nitrogen dioxide is a mild corrodant and may, by itself, exhibit a weak passivating effect on carbon-steel. However, it is suggested that the significance of nitrogen dioxide as an atmospheric corrodant is as a synergist to the corrosive effects of sulfur dioxide.

The effects of sunlight should similarly alter the behavior of exposed iron surfaces as it does for zinc and copper. Like nitrogen dioxide, sunlight should synergistically accelerate corrosion by sulfur dioxide.

Alternate surface wetting occurs with precipitation, fog, and dew events and would dramatically accelerate corrosion and degradation of surface coatings. Accordingly, surface wetting studies should be conducted.

It is therefore recommended that similar studies to these be undertaken using a matrix of humidity, nitrogen dioxide, and sulfur dioxide exposure conditions. The objectives of such studies should be (in order):

- to determine the nature and extent of the synergism between nitrogen dioxide and sulfur dioxide;
- to establish the conditions for extending the use of the surface microcells to field studies;
- to determine the effects of alternate wetting; and
- to determine the effects of sunlight.